Electrostatic Binding of Metal Complexes to Electrode Surfaces Coated with Highly Charged Polymeric Films

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Previous reports in which metal complexes have been attached to electrode surfaces coated with polymeric molecules have depended upon the formation of covalent or coordination bonds in the attachment procedure (1-4). Such schemes can be quite successful but depending, as they do, on rather specific surface chemistry, they are not applicable to as wide a variety of metal complexes as might be desirable. We have observed that coating graphite electrodes with polymers bearing charged ionic groups produces surfaces which strongly bind multiply-charged metal complexes bearing charges opposite to that on the attached ionic polymer. By exploiting this observation it is entirely possible that virtually any desired metal ion can be attached in large quantities to electrode surfaces by coordinating the metal ion with ligands that produce a multiply-charged complex ion.

EXPERIMENTAL

The source and mounting of the pyrolytic graphite electrodes and procedures for coating them with adherent films of poly (4-vinylpyridine) (M.W.= 7.4 x 10^5) have been previously described (1,4) along with the electrochemical measuring techniques employed. Potentials are quoted vs. a sodium chloride saturated calomel electrode.

RESULTS AND DISCUSSION

The effective pK values of polyelectrolytes such as poly (4-vinylpyridine) (PVP) depend somewhat upon molecular weight. However, it is likely that PVP is largely protonated at pH values below ca. 3 and essentially neutral at

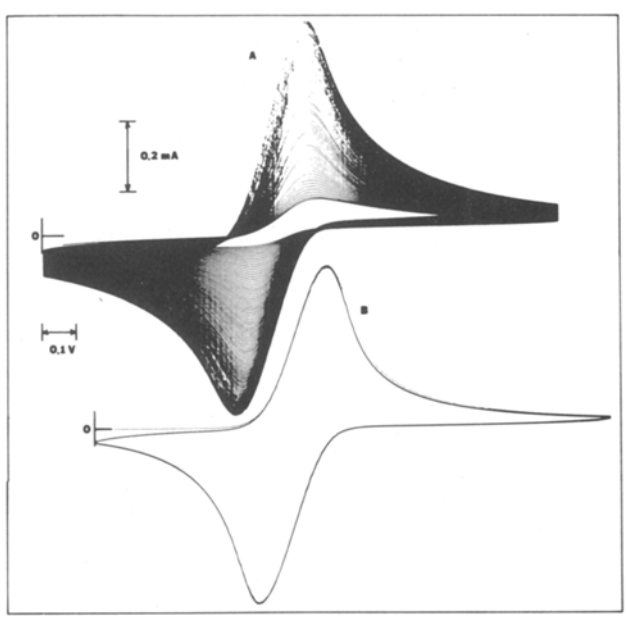

Figure 1: A - Cyclic voltammograms of 5 mM $Fe(CN)_6^{3-}$ at a pyrolytic graphite electrode (0.17 cm^2) coated with 4.6 x 10^{-7} moles cm^{-2} of pyridine as PVP. Supporting electrolyte: 0.2 M CF_3COONa at pH 3.8. The potential was cycled continuously at 200 mV s^{-1} between +0.8 and -0.7 volt. The voltammogram reached a steady state after 20 minutes of cycling. B - Cyclic voltammogram resulting after the electrode used in A was washed with water and replaced in 0.2 M CF_3COONa at pH 2.9.

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pH values above ca. 8 (5). To prepare a highly positively charged electrode surface a graphite electrode was coated with PVP and exposed to supporting electrolyte at pH 3.8. The resulting electrode was used to record the series of cyclic voltammograms for $Fe(CN)_6^{3-}$ shown in Figure 1A.

The peak current obtained immediately after the electrode was introduced into the solution is somewhat smaller than the current at uncoated electrodes because the polymer film retards the $Fe(CN)_6^{3-/4-}$ electrode reaction somewhat (4). However, in sharp contrast with uncoated electrodes, the voltammetric currents increase as the potential is cycled continuously and they reach extraordinarily large values. (The currents also increase, although somewhat less rapidly, if the electrode potential is not cycled.) If the electrode is removed from the solution, rinsed and transferred to an acidic solution containing only supporting electrolyte the voltammogram shown in Figure 1B is obtained and its magnitude is virtually unaffected by repeated cycling for periods up to one hour. The voltammogram in Figure 1B disappears if the electrode is removed, washed with electrolyte at pH 10 and replaced in the supporting electrolyte. These observations seem clearly to demonstrate that the protonated PVP film on the electrode surface preferentially incorporates the multiply-charged ferricyanide as the counter ion, even though much larger concentrations of singly-charged trifluoroacetate anions are present in the supporting electrolyte. The behavior is quite analogous to that of polyelectrolytes in homogeneous solutions under conditions where the polyion is highly charged (6). The fact that multiply-charged counter ions incorporated into PVP films are not replaced rapidly by ion exchange upon exposure to simple univalent electrolytes containing none of the multiply-charged ion indicates that a significant activation barrier impedes the break-up of the electrostatic binding within the polyionic film.

Figure 2 emphasizes this point for the case in which the dinegative anion, $IrCl_6^{2-}$, is held electrostatically within a protonated PVP film. Initially after transfer of the coated electrode from the solution of $IrCl_6^{2-}$ to a solution containing only supporting electrolyte at pH 2.8 there is a fairly rapid loss of a fraction of the $IrCl_6^{2-}$ from the surface - presumably from the portion of the polymer most accessible to the electrolyte. However, after a few minutes of repetitive scanning the voltammogram settles down to the one shown in Figure 2 which undergoes no further change during several additional minutes of scanning. If the pH of the supporting electrolyte is raised to 4.5 the release of $IrCl_6^{2-}$ from the surface resumes as revealed by a steadily diminishing voltammetric response.

The extent of the electrostatic attachment is not related simply to the charge carried by the counter ion being attached. For example, exposing a PVP coated electrode to a solution containing both 5 mM $Fe(CN)_6^{3-}$ and 5 mM $IrCl_6^{2-}$ leads to greater binding of the less highly charged anion. Thus, chemical differences among the incorporated ions appear to modulate purely electrostatic factors in controlling the extent of incorporation.

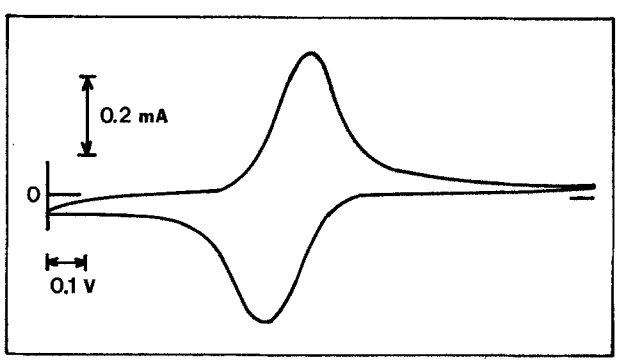

Figure 2: Steady-state cyclic voltammogram for an electrode coated with 4.6×10^{-7} moles cm^{-2} of PVP, soaked in a 5mM solution of $(NH_4)_2IrCl_6$ at pH 2.8 (CF_3COOH) for 60 seconds, rinsed with water and transferred to supporting electrolyte solution (0.2 M CF_3COONa at pH 2.6). Scan rate: 200 mVs^{-1}. Potential range: +1.3 to -0.1 volt.